THE DEVELOPMENT OF URANIUM CARBIDE AS A NUCLEAR FUEL

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SUMMARY

The objective of the work described in this report was the determination of the effects of carbon content and fabrication method on irradiation stability, thermal conductivity and hot hardness of uranium carbide. Hypostoichiometric and stoichiometric uranium carbide prepared by both powder metallurgy and skull casting and hyperstoichiometric cast carbide were tested.

The preparation of 12% enriched uranium carbide specimens for irradiation testing was completed. Sintered specimens were 98% of theoretical density for hypostoichiometric uranium carbide and 92 to 93% of theoretical for stoichiometric uranium carbide. All cast specimens were above 98.7% of theoretical density. Five different specimens, 4.4 and 4.8 ± 0.1 w/o carbon, cast material and sintered material, and 5.2 ± 0.1 w/o carbon, cast uranium carbide, were canned separately in niobium-1 w/o Zr and inserted into each of three capsules. The fuel specimens in capsule UNC-1-2 were contained in a sodium bond. This capsule was removed after 15,000 MW-d/ton U burnup in the MTR and is now undergoing post-irradiation examination. Capsule UNC-1-1 also has sodium bonded specimens but will be irradiated to 30,000 MW-d/ton U (anticipated to be about July 1963).

The specimens in capsule UNC-1-3 were canned using an interference fit between cladding and fuel. This capsule was removed from the MTR after 14,440 MW-d/ton U burnup and is awaiting post-irradiation examination.

Fuel surface temperatures ran in the range of 650 to 870°C and center-line temperatures were calculated at about 1050 to 1100°C.

Specimens were prepared for thermal expansion, thermal conductivity, and hot hardness measurements. These properties are being determined from room temperature to 1000°C for multiple specimens of each test condition. Thermal conductivity and hot hardness measurements are just getting under way and no data are available at this time. Thermal expansion of uranium carbide from room temperature to 1000°C was found to be 12.4×10^{-6} per °C for 4.4 w/o carbon sintered material, and 11.5×10^{-6} per °C for 4.7 w/o carbon cast material. Additional data on thermal expansion are currently being obtained.

Out-of-pile compatibility tests were run at 815°C for 260 hr for hypo and hyperstoichiometric uranium carbide with niobium-1 w/o Zr cladding and with sodium as the bonding material. The hypostoichiometric material was prepared by powder metallurgy; the hyperstoichiometric carbide was made by skull casting. These tests showed some surface damage of the uranium carbide at both levels of carbon content. This damage was in the form of oxidation of free uranium in the case of the low carbon material and appeared as small cracks and chipping in the case of hyperstoichiometric material. Evidence of carburization to a depth of 0.0001 in. was noticed at the surface of the cladding used with the hyperstoichiometric uranium carbide. The evidence was not conclusive and no decarburization of the fuel was observed.

Exposure tests of cast uranium carbide specimens with as-cast as well as ground surfaces and at three levels of carbon content, 4.5, 4.7, and 5.3 w/o, were performed. Satisfactory resistance to corrosion was observed for 4.5 and 4.7 w/o carbon material exposed to laboratory air for about 10 months, but the 5.3 w/o carbon specimens, both as-cast and ground surfaces, showed transverse cracking after five months. All specimens stored in vacuo showed some surface attack and slight pitting starting after five months storage but no cracking has been observed. Carbon content of these specimens did not appear to have any effect

on corrosion behavior. These tests are still in progress, and similar tests for sintered material will be started shortly.

Additional information was gained on the reproducibility of the skull casting method during preparation of castings for property studies. This information clearly indicated that stoichiometric UC castings containing less than 200 ppm oxygen and 100 ppm nitrogen could be consistently made to 4.8 ± 0.1 w/o carbon using 4.6 w/o carbon feed material obtained by solid state reaction of UO_2 with graphite. A homogeneous skull of 4.8 w/o carbon was required. Similar reproducibility of casting carbon content was achieved at other carbon levels. Methods for minimizing certain casting defects were also found.

The density of sintered uranium carbide has been found to be strongly dependent upon carbon content. Carbon powder (4.3 to 4.4 w/o) was sintered to 96 to 98% of theoretical density, with little or no change in carbon content, while 4.5 w/o carbon powder was sintered to stoichiometric UC at 90 to 93% of theoretical density. The change in carbon content of the latter appears to be due to uranium volatilization at the 1800°C sintering temperature; sintering of the low carbon material was performed at 1200°C.

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1. INTRODUCTION

The participation of United Nuclear Corporation in the Fuel Cycle Development Program includes development of methods to prepare uranium carbide by powder metallurgy and skull arc casting, and determination of certain properties of carbide fabricated by both methods at various carbon levels. The first and second annual reports^{1,2} described the work performed in this laboratory from May 1, 1959 to August 31, 1961. This work dealt mainly with establishing conditions for making a high density, high purity product by powder metallurgy and skull arc casting.

These efforts culminated in the development of methods for preparing sintered uranium carbide of substoichiometric and stoichiometric composition to 98 and 93% of theoretical density, respectively. After experimenting with propane and methane, propane was preferred as the carburizing gas to prepare the carbide powder because of its lower cost and higher purity as commercially available. A low temperature sinter, at about 1200°C, was used for the low carbon material (4.4 w/o); and sintering at 1800°C for three hours was employed for preparation of stoichiometric uranium carbide. Nitrogen contents of less than 500 ppm and oxygen contents of less than 1000 ppm are consistently attainable. The development of the skull arc casting method resolved the question of charge material in favor of uranium carbide made by reacting UO_2 -graphite compacts at 1700°C for two hours. Castings from 7/16 in. to 3/4 in. diameters were successfully made. The cast material was consistently below 400 ppm oxygen and 100 ppm

nitrogen. For a small lot of castings, carbon control had been established as feasible, but certain casting defects (radial microcracking in large diameter castings and pipe in all castings) reduced the efficacy of this method. The work accomplished up to August 31, 1961 indicated that further reduction of oxygen, minimizing or eliminating radial cracking, and reproducibility of carbon content for production quantities of castings, was well within reach.

The final part of the program, which was the primary concern of this past year's effort, was the determination of the effect of carbon content and method of fabrication (powder metallurgy and casting) on irradiation stability, thermal expansion, thermal conductivity, and hot hardness of uranium carbide. This report covers the progress made over the past year in preparing test specimens and in carrying out the test programs. For all determinations the variables regarding fabrication and carbon content were the same and are as follows:

Powder Metallurgy - 4.4 and 4.8 ± 0.1 w/o carbon

Casting - 4.4, 4.8, and 5.2 ± 0.1 w/o carbon.

It was felt that the carbon levels chosen were sufficiently spread out to truly reflect the effects of the presence of a second phase compared with stoichiometric material; and the tolerance for each composition was considered small enough not to introduce ambiguity in interpreting the data, while reflecting what could reasonably be achieved and reproduced by the techniques developed at United Nuclear Corporation during the previous two years.

Out-of-pile compatibility tests of the materials system used for the irradiation test program and exposure tests of cast uranium carbide are also described in the following text.

2. EXPERIMENTAL WORK

2.1 IRRADIATION PROGRAM

The preparation of the uranium carbide specimens was performed by United Nuclear, and encapsulation, surveillance of the irradiation testing, and post-irradiation examination were subcontracted to Battelle Memorial Institute.* The materials system chosen, aside from the uranium carbide, consisted of niobium-1% zirconium for the fuel container and sodium as the heat transfer medium. The design conditions included a fuel surface temperature of 750°C, centerline temperature of 1250°C, fission heat rate of 1.5×10^6 Btu/hr-ft² and a fuel burnup of 15,000 and 30,000 MW-d/ton U. The fuel specimen geometry chosen was 0.375 diam $\times$ 0.750 long. Three capsules containing one each of the following specimens were to be irradiated.

4.4 $\pm$ 0.1 w/o carbon sintered

4.4 $\pm$ 0.1 w/o carbon cast

4.8 $\pm$ 0.1 w/o carbon sintered

4.8 $\pm$ 0.1 w/o carbon cast

5.2 $\pm$ 0.1 w/o carbon cast

Five similar fuel specimens were to be prepared as control samples. The fuel was of 12% enrichment.

*The work performed by BMI is under the supervision of J.E. Gates and R.F. Dickerson.

2.1.1 Compatibility Study

It was decided to run a short term, out-of-pile compatibility test prior to encapsulation of the actual irradiation test specimens to insure that the materials system chosen was a good one. Of principal concern were the effects of sodium on uranium carbide and on carburization of the cladding due to carbon transfer from the fuel. Prototype specimens of depleted uranium carbide made to the same specifications set up for the irradiation test specimens were used for the compatibility study. The fuel specimens were made at United Nuclear Corporation and encapsulation, testing, and metallographic examinations were performed at Battelle Memorial Institute.

The containers were fabricated from 0.030 in. thick niobium-1 w/o Zr. A gap of 0.020 in. between cladding and fuel was filled with freshly gettered sodium. The carbide specimens, 4.4 w/o carbon sintered material and 5.2 w/o carbon cast material, were centered in the fuel container with a 0.015 in. diameter molybdenum wire spiraled around the fuel specimen. The fuel containers were loaded under a helium atmosphere and heliarc welded.

The test was carried out at 815°C for 260 hr in a vacuum furnace. It was felt that the 260 hr test would be sufficient to indicate any tendencies toward incompatibility which might occur at the irradiation test design temperature at the fuel surface (750°C), and would still be short enough to permit examination prior to encapsulation of the irradiation test specimens.

The microstructure of the 4.4 w/o carbon sintered specimen prior to the 260 hr test is shown in Fig. 1. The matrix is UC with free uranium in the grain boundaries and dispersed throughout the grains. Fig. 2 shows this basic microstructure unchanged after the test. A close examination of the surface revealed, however, that the uranium in the grain boundaries had been attacked, apparently oxidized, to a depth of about 0.001 in. (Fig. 3).

Fig. 1 — Microstructure of 4.4 w/o carbon sintered uranium carbide at surface of specimen, prior to compatibility study. Etchant: nitric acid, acetic acid, water. Magnification: 100×

Fig. 2 — Microstructure of 4.4 w/o carbon sintered uranium carbide at surface of specimen, after 260 hr at 815°C in sodium contained by niobium-1 w/o Zr alloy. Etchant: nitric acid, acetic acid, water. Magnification: 100×

Fig. 3 — Cross-sectional view of 4.4 w/o carbon sintered uranium carbide specimen showing grain boundary attack at surface of specimen, after 260 hr at 815°C in sodium contained by niobium-1 w/o Zr alloy. Etchant: nitric acid, acetic acid, water. Magnification: 750×

The microstructure of the hyperstoichiometric material exhibited no change as a result of the 260 hr treatment, but the surface of the specimen did show microcracks (Fig. 4).

No interaction of cladding with fuel was evident in the case of the hypostoichiometric material. However, microexamination revealed evidence of carburization at the surface of the 5.2 w/o carbon fuel cladding to a depth of about 0.0001 in. (Fig. 5). This microstructural evidence could not be positively identified as a carbide of niobium, and it is noteworthy that no decarburization of the uranium carbide was seen metallographically.

The cause of the attack of uranium in the hypostoichiometric uranium carbide seen at the surface of the specimen could not be determined conclusively, but was believed to be oxidation. The sodium in contact with the fuel had been gettered with zirconium chips prior to testing to reduce its oxygen content to low levels, and it was not considered a likely source of sufficient oxygen to account for the surface attack seen. Other possible sources of oxygen are surface contamination, and oxygen in the helium atmosphere used in the dry box during encapsulation.

Surface cracking of the hyperstoichiometric carbide may have been the result of corrosion; cracking of a somewhat similar nature has been attributed by other investigators to attack by moisture.³

Although none of the above effects were considered serious, it was felt that the possibility of sodium being responsible for some deleterious effects on the fuel or cladding during the actual irradiation testing did exist. Therefore, to develop the best data from irradiation tests, it was decided to include one capsule utilizing an interference fit between fuel and clad, as well as two capsules employing the sodium bond. No other changes were deemed advisable.

(a) Uranium-5.2 w/o carbon specimen surface prior to compatibility study

(b) Above sample after 260 hr at 815°C in sodium contained by niobium-1 w/o Zr alloy (note cracking at surface).

Fig. 4 — Photomicrographs of cast 5.2 w/o carbon specimen at surface before and after compatibility study. Etchant: nitric acid, acetic acid, water. Magnification: 100×

Fig. 5 — Surface of niobium-1 w/o Zr alloy cladding in contact with sodium during compatibility study. Surface layer about 0.0001 in. thick is believed to be carburization. Magnification: 250×

2.1.2 Preparation of Irradiation Test Specimens

Powder Metallurgy

Twelve percent enriched uranium derby was obtained from the Chemical Division of United Nuclear Corporation. The derby was sectioned into three 600 gm charges and one 100 gm charge. Just before loading a charge in the retort, it was pickled in 50 v/o nitric acid, rinsed successively in water and alcohol, and dried. After purging the retort with argon, and flushing with hydrogen, the uranium was hydrided at 200°C. Carburizing was carried out using chemically pure tank propane at a flow rate of two liters per minute.

It was intended to prepare 4.4 and 4.5 w/o carbon uranium carbide powder to make, respectively, 4.4 ± 0.1 and 4.8 ± 0.1 w/o carbon sintered bars. It was known that the sintering temperature for the lower carbon material was low enough so that the carbon content did not change. The high temperature sintering of the 4.5 w/o carbon powder resulted in a net carbon gain of about 0.3 w/o, apparently caused by uranium volatilization. Heat-up rate, holding temperature, and hold time had been previously established in experimental runs using depleted uranium. Data for the four carburizing runs made using enriched material are shown in Table 1. Run E-3-488381 greatly exceeded the intended carbon level and was not used for preparing irradiation specimens. The excessively high carbon content of run E-3-488381 could not be explained on the basis of results using similar parameters in earlier work with depleted uranium. Run E-4-488397 was made to produce very low carbon material to blend with E-3-488392 and thus bring the carbon content down to a level suitable for preparing 4.4 ± 0.1 w/o carbon sintered bars.

The powder from run E-1-488377 (4.51 w/o carbon) was mixed with a 2½% solution of camphor in petroleum ether to yield carbide containing 1/2 w/o camphor. After blending and drying, the powder was compacted at 50 tsi pressure to form rectangular compacts, nominally $1/2 \times 1/2 \times 2\frac{1}{2}$ in. Three bars, weighing about 100 grams each, were then sintered at about 1800°C for three hours in vacuo.

Table 1 — Carburization of 12% Enriched Uranium by the Propane Reaction

Run No.	Charge Weight, g	Carburizing Time, minutes		Carburizing Temperature, °C	Carbon* Content, w/o
		To Attain Temperature	Time at Temperature		
E-1-488377	612.2	88	30	601	4.51
E-2-488381	610.4	114	40	624	5.15
E-3-488392	608.8	76	20	601	4.50
E-4-488397	125.0	53	Not held	500	2.68

*Analyzed total carbon content.

Data for green compacts are shown in Table 2. Density of the sintered bars was 12.4 g/cm^3 . All handling of powder and unsintered compacts was done in an argon dry box. The total carbon content of the sintered bars was 4.86 w/o showing a gain of 0.35 w/o carbon presumably resulting from uranium loss during sintering.

To prepare the hypostoichiometric sintered uranium carbide, powder from run E-3-488392 was reduced from 4.50 w/o carbon to 4.31 w/o carbon by additions of a calculated amount of material from run E-4-488397 (2.68 w/o carbon). After adding 1/2 w/o camphor (2½% solution of camphor in petroleum ether) and suitable mixing, the powder was compacted at 50 tsi. Three compacts, each weighing about 100 grams, were sintered at 1200°C for three hours in vacuo. Data for green compacts are shown in Table 3. The sintered density, determined by immersion in carbon tetrachloride, was 13.7 g/cm^3 . The total carbon content was 4.31 w/o showing no change in carbon during the sintering.

It is noteworthy that in the course of preparing the hypostoichiometric sintered uranium carbide, three separate bars, each of different carbon content, were sintered at 1200°C in vacuo for three hours after compacting at 50 tsi. The material for these bars came from run E-1-488377 (4.51 w/o carbon) and two lots of E-3-488392 (4.50 w/o carbon) diluted in carbon by different additions of E-4-488397 (2.68 w/o carbon) to form 4.44 w/o carbon uranium carbide powder and 4.31 w/o carbon uranium carbide powder. As the carbon content increased from 4.31 to 4.44 to 4.51 w/o, the density correspondingly dropped from 13.62 g/cm^3 (97% theoretical) to 13.13 g/cm^3 (94% theoretical) to 12.10 g/cm^3 (87% theoretical). The latter two bars were not used for preparation of irradiation test specimens.

The sintered bars were then machined to make four specimens 0.375 ± 0.001 in. diameter by 0.750 ± 0.005 in. long of each composition. Grinding was performed using a silicon carbide 60-grit wheel and a high flashpoint mineral seal oil. Finished ground powder metallurgy specimens are shown in Figs. 6 and

**Table 2 — Green Compacts made from Enriched Powder
E-1-488377**

Bar No.	Compact Weight, g	Compact Dimensions, in.	Density, g/cm ³ *
E-1-4	92.2	0.505 × 0.532 × 2.540	8.2
E-1-5	93.3	0.515 × 0.532 × 2.538	8.2
E-1-6	92.5	0.510 × 0.534 × 2.540	8.2

*Volume determined from bar dimensions.

**Table 3 — Green Compacts from Blend of Enriched Powder,
Runs E-3-488392 and E-4-488397**

Bar No.	Compact Weight, g	Compact Dimensions, in.	Density, g/cm ³ *
E-6-2	96.7	0.521 × 0.533 × 2.535	8.4
E-6-3	95.9	0.517 × 0.532 × 2.535	8.4
E-6-4	96.8	0.522 × 0.532 × 2.536	8.4

*Volume determined from bar dimensions.

(a) Hypostoichiometric sintered uranium carbide specimens after machining. Actual size.

(b) Longitudinal view of one specimen at 4×

(c) Transverse view of specimen shown at left. Magnification 4×

Fig. 6 — Sintered uranium carbide irradiation test specimens (4.31 w/o carbon) after grinding to finished size

(a) Stoichiometric sintered uranium carbide specimens after machining – actual size

(b) Longitudinal view of single specimen at 4×

(c) Transverse view of specimen shown at left. Magnification 4×

Fig. 7 — Sintered uranium carbide irradiation test specimens (4.86 w/o carbon) after grinding to finished size

7. Metallography was performed on a cross section of each bar, and a sample of each bar left after machining was used for additional analyses for free carbon, oxygen, and nitrogen. Density measurements were made of all finished specimens. Table 4 summarizes analytical, density, and dimensional determinations. Figs. 8 and 9 show representative microstructures of substoichiometric and stoichiometric UC at magnifications of 100 and 250 $\times$.

The specimens were then sealed in Tygon tubing in an argon atmosphere and the tubes were packed for shipment to Battelle with desiccant in polyethylene bottles sealed in an argon dry box.

Skull Casting

In order to prepare 12% enriched cast uranium carbide specimens for irradiation testing, it was necessary to first make a 5 to 7 kg skull of 12% enriched uranium carbide. The skull was prepared by melting reacted UO_2 -graphite charges in the skull furnace. The charges were made by blending 12% enriched uranium dioxide obtained from the Chemical Division of United Nuclear Corporation with National Carbon Grade 48 graphite, compacting the mixture at 30 tsi to form pellets $1/2$ in. diameter $\times$ $3/8$ in. thick, and reacting the pellets. Seven charges, each initially comprised of 1000 grams of uranium dioxide and 128.5 grams of graphite were required to make the skull. This oxide-to-graphite ratio was calculated to yield a product containing 4.3 w/o carbon in accordance with the reaction $\text{UO}_2 + 3\text{C} \rightarrow \text{UC} + 2\text{CO}$. The reaction of the UO_2 -graphite charges was carried out in an induction furnace at 1700 $^\circ\text{C}$ for two hours at a pressure of 5 to 15 in. Hg absolute, maintained by throttling a mechanical vacuum pump to pull off the evolving CO. The reacted charges were taken from the induction furnace and transferred to the skull furnace in a crucible sealed under argon. Melting of the seven charges into a homogeneous skull and formation of a skull cavity required seven melts.

The charges used to make castings for the 4.4, 4.8, and 5.2 ± 0.1 w/o carbon irradiation test specimens consisted of 900 grams of uranium dioxide and sufficient graphite to yield 4.3, 4.7, and 5.0 w/o carbon, respectively, after reaction.

Table 4 — Description of Irradiation Test Specimens Made by Powder Metallurgy

Specimen No.	Chemical Analyses, w/o				Dimensions, in.		Density, g/cm ³	% of Theoretical
	Total Carbon	Free Carbon	Nitrogen	Oxygen	Diameter	Length		
E-6-2B	4.31	None	<0.01	0.04	0.3758	0.7538	13.76	98.1†
E-6-3	4.31	None	<0.01	0.04	0.3755	0.7540	13.77	98.1†
E-6-4A	4.31	None	<0.01	0.04	0.3756	0.7540	13.77	98.1†
E-6-4B*	4.31	None	<0.01	0.04	0.3753	0.7534	13.77	98.1†
E-1-4A	4.86	None	<0.01	0.08	0.3750	0.7540	12.51	91.9‡
E-1-4B	4.86	None	<0.01	0.08	0.3750	0.7540	12.68	93.2‡
E-1-5*	4.86	None	<0.01	0.08	0.3750	0.7490	12.57	92.4‡
E-1-6	4.86	None	<0.01	0.08	0.3760	0.7530	12.61	92.6‡

*Control specimens — not assembled in capsules.

†Archimedes density using carbon tetrachloride as displacement medium to measure volume.

‡Archimedes density using mercury as displacement medium to measure volume.

(a) Center of specimen – 100×

(b) Surface of specimen – 100×

(c) Center of specimen – 250×

Fig. 8 — Microstructure of 4.31 w/o carbon uranium carbide irradiation test specimen prepared by powder metallurgy. Etchant: nitric acid, acetic acid, water.

(a) Center of specimen – 100×

(b) Surface of specimen – 100×

(c) Center of specimen – 250×

Fig. 9 — Microstructure of 4.86 w/o carbon uranium carbide irradiation test specimen prepared by powder metallurgy (note presence of UC_2 platelets near specimen surface).
Etchant: nitric acid, acetic acid, water

A reacted charge was placed in the skull cavity after the skull was verified to be the right composition for the desired casting carbon content. The charge was then melted using a standard five-minute melt cycle and a pour was made into a three-mold cluster yielding three 7/16 in. diameter by 6 in. long castings.² After the castings were verified by chemical analysis to be the proper carbon content, the skull was readjusted for the next carbon level by additions of uranium dioxide or graphite, as required, and sufficient homogenizing melts were made to incorporate the additive homogeneously.

In order to prepare the three required compositions four melts were required; one set of castings exceeded the desired carbon content and had to be recycled. Carbon content was determined initially by analysis of a sample from one casting of the three-casting cluster, but subsequently all castings used for preparation of test specimens were individually analyzed for total carbon. Table 5 shows the carbon content of cast material used for the irradiation test program.

The cast rods were then ground to finished size using an 80-grit silicon carbide wheel and a high flash point mineral seal oil for lubricant. Finished ground cast specimens are shown in Figs. 10, 11 and 12. Metallographic examination was made of specimens representing each carbon level (Figs. 13, 14, 15), and density and dimensional measurements were made of each test specimen (Table 5).

The finished specimens were then packaged for shipment to Battelle in the same manner described previously for the powder metallurgy specimens.

2.1.3 Encapsulation of Irradiation Test Specimens

Five fuel specimens canned separately in niobium-1% zirconium were required for each of three instrumented capsules. The five fuel specimens in each capsule were as follows:

4.4 $\pm$ 0.1 w/o carbon sintered

4.8 $\pm$ 0.1 w/o carbon sintered

Table 5 — Description of Irradiation Test Specimens Made by Skull Arc Casting

Specimen No.	Chemical Analyses, w/o				Dimensions, in.		Density, g/cm ³ †	% of Theoretical
	Total Carbon	Free Carbon	Nitrogen	Oxygen	Diameter	Length		
19D-728-1A	4.45	None	<0.01	0.018	0.3754	0.7540	13.90	99.9
19D-728-1B	4.45	None	<0.01	0.018	0.3753	0.7535	13.94	100
19D-728-2B*	4.44	None	<0.01	0.018	0.3756	0.7530	13.84	99.5
19D-728-3A	4.44	None	<0.01	0.018	0.3749	0.7475	13.92	100
19D-709-1C	4.70	None	<0.01	0.003	0.3756	0.7517	13.68	99.7
19D-709-2A	4.71	None	<0.01	0.003	0.3751	0.7535	13.64	99.4
19D-709-2B	4.71	None	<0.01	0.003	0.3759	0.7515	13.58	99.0
19D-709-2C	4.71	None	<0.01	0.003	0.3756	0.7497	13.61	99.2
19D-715-1A*	5.19	None	<0.01	0.03	0.3743	0.7510	13.36	99.1
19D-715-2A*	5.20	None	<0.01	0.03	0.3751	0.7460	13.32	98.8
19D-715-2B	5.20	None	<0.01	0.03	0.3755	0.7535	13.36	99.1
19D-715-3A	5.21	None	<0.01	0.03	0.3748	0.7480	13.40	99.4
19D-715-3B	5.21	None	<0.01	0.03	0.3745	0.7515	13.40	99.4

*Control specimens — not assembled in capsules.

†Density determined by Archimedes Method using carbon tetrachloride as the displacement medium for measuring volume.

(a) Hypostoichiometric cast uranium carbide specimens after machining – actual size

(b) Longitudinal view of single specimen at 4×

(c) Transverse view of specimen shown at left. Magnification 4×

Fig. 10 — Cast uranium carbide irradiation test specimens (4.4 w/o carbon) after grinding to finished size

(a) Stoichiometric cast uranium carbide specimens after machining – actual size

(b) Longitudinal view of one specimen at 4×

(c) Transverse view of specimen shown at left. Magnification 4×

Fig. 11 — Cast uranium carbide irradiation test specimens (4.7 w/o carbon) after grinding to finished size

(a) Hyperstoichiometric cast uranium carbide specimens after machining — actual size

(b) Longitudinal view of one specimen at 4×

(c) Transverse view of specimen shown at left. Magnification 4×

Fig. 12 — Cast uranium carbide irradiation test specimens (5.2 w/o carbon) after grinding to finished size

(a) Center of specimen – 100×

(b) Surface of specimen – 100×

(c) Center of specimen – 250×

Fig. 13 — Microstructure of 4.4 w/o carbon uranium carbide irradiation test specimen prepared by skull casting. Etchant: nitric acid, acetic acid, water.

(a) Center of specimen - 100×

(b) Surface of specimen - 100×

(c) Center of specimen - 250×

Fig. 14 — Microstructure of 4.7 w/o carbon uranium carbide irradiation test specimen prepared by skull casting. Etchant: nitric acid, acetic acid, water.

(a) Center of specimen – 100×

(b) Surface of specimen – 100×

(c) Center of specimen – 250×

Fig. 15 — Microstructure of 5.2 w/o carbon uranium carbide irradiation test specimen prepared by skull casting. Etchant: nitric acid, acetic acid, water.

4.4 $\pm$ 0.1 w/o carbon cast

4.8 $\pm$ 0.1 w/o carbon cast

5.2 $\pm$ 0.1 w/o carbon cast

After additional metallographic examination and density and dimensional determinations of the fuel specimens were made by Battelle, the fuel specimens were canned in a helium atmosphere dry box. For those specimens utilizing a sodium bond between fuel and cladding, the fuel container was machined to 0.415 in. inside diameter, allowing 0.020 in. clearance between fuel and cladding (Fig. 16). A void space filled with helium was provided at one end of the can to reduce end heat losses. A predetermined quantity of freshly gettered sodium, sufficient to completely immerse the fuel specimen, was placed in the can, and the fuel specimen with a 0.015 in. diameter molybdenum wire spiraled around it for centering purposes, was then inserted. The design provided for an expansion space in the fuel container above the sodium to accommodate fission gases which might escape from the fuel during irradiation. The end caps were heliarc welded in place and the container was heated to melt the sodium and allow the fuel to be submerged in liquid sodium. The can was then checked for leakage and radiographed to verify that the fuel was fully covered by sodium. A typical canned specimen is shown in Fig. 17.

The specimens which were canned without a sodium bond required only insertion of spacers and fuel prior to heliarc welding the end caps. In order to compensate for the absence of sodium, the fuel container was redesigned to allow for a half-mil clearance between fuel and cladding at room temperature, estimated to give a 0.001 in. interference fit at operating temperature (Fig. 18).

The three capsules were assembled, each capsule containing five canned specimens. Fig. 19 is a picture of the capsule components before assembly. The sodium-bonded specimens were loaded in capsules UNC-1-1 and UNC-1-2; the specimens clad with an interference fit were placed in capsule UNC-1-3.

Fig. 16 — Design of fuel container using a sodium bond between fuel and cladding material

Fig. 17 — Longitudinal view of welded fuel container.
Cladding is niobium-1 w/o Zr heliarc welded at ends.
Magnification: 2×

Fig. 18 — Design of fuel container using an interference fit between fuel and cladding material

UNC 1-3 CAPSULE PARTS

Fig. 19 — Capsule components before assembly

2.1.4 Irradiation Testing

The three capsules were inserted in the MTR in February and March 1962. During irradiation, the temperature was monitored by control thermocouples located at the outer surface of each fuel can. A temperature of 1200°F at the control thermocouple corresponds to a fuel surface temperature of about 800°C. Auxiliary heating was used as required. On October 29, 1962, capsules UNC-1-2 and UNC-1-3 were removed and were sent to Battelle for post-irradiation examination. The fuel burnup was estimated to be 15,000 MW-d/ton U for UNC-1-2 and 14,400 MW-d/ton U for UNC-1-3. Fuel surface temperatures for the three capsules ranged between 700 and 800°C for most of the test with temperatures as low as 650°C and as high as 870°C occasionally reported. The fuel centerline temperatures were calculated to be between 1050 and 1100°C. Capsule UNC-1-1 will remain in the MTR until the specimens in this capsule receive a burnup of 30,000 MW-d/ton U. This burnup should be achieved by July 1963.

2.2 PHYSICAL PROPERTY DETERMINATIONS

As in the case of the irradiation test program, the physical property determinations of uranium carbide were made to establish the effects of carbon content and fabrication method on the properties to be tested.

The methods of preparation of test specimens for thermal expansion and hot hardness determinations essentially followed those employed for making the irradiation test specimens. The sintered thermal conductivity specimens, however, were prepared by pressing carbide powder to form green cylindrical compacts 3/4 in. diameter by 1½ in. long which, after sintering, were machined to right cylinders 1/2 in. diameter by 3/4 in. long. Densities of powder metallurgy specimens have been 90 to 93% of theoretical for stoichiometric material and 96 to 98% of theoretical for 4.3 to 4.4 w/o carbon uranium carbide. Cast thermal conductivity specimens were machined from 3/4 in. diameter castings.

During preparation of the cast specimens, it was found that the desired

carbon content could be consistently met to ± 0.1 w/o using reacted charge material with a carbon content 0.2 w/o below the skull. The skull was of the same carbon content as that desired for the casting. The carbon content of the reacted charge was based solely on proportions of UO_2 with graphite in the original mix. The charges were not reacted to completion; i.e., substantial amounts of oxide and graphite were present in the products used for melting.

Radial cracking associated with thermal stresses during cooling had previously been noted in castings larger than 1/2 in. diameter. This cracking was essentially eliminated in recent castings by keeping the sprue small and insulating the mold when necessary. Castings below about 4.5 w/o carbon tended to develop transverse cracking believed to be hot tears. This cracking was minimized, though not eliminated, by coating the mold with carbide to prevent casting interaction with the mold.* This interaction had seriously constrained the casting during solidification; and, it is believed, greatly encouraged hot tearing.

Oxygen contents of the cast carbide have been running well below 200 ppm and are averaging about 90 ppm. Nitrogen in cast material has always been below 100 ppm.

2.2.1 Thermal Expansion

The expansion characteristics of uranium carbide are being determined in the temperature range from about 25 to 1000°C, in vacuo, using a Leitz dilatometer with a modified vacuum chamber.

The data are obtained with the aid of a mirror galvanometer which moves a light source horizontally as a function of temperature while the expansion of the specimen moves the light along the ordinate. The curve, which is the resultant of these two displacements, is traced on light-sensitive film and thereby provides a direct recorded plot of expansion vs temperature for each specimen. The speci-

*The carbide coating was made by applying a mix of UO_2 , graphite, water, and a suspending agent to the mold ID, drying and heating at temperatures sufficient to reduce the oxide and to form carbide.

mens are nominally 8 mm diameter by 25 mm long. Triplicate specimens of each of the five test conditions are being run. The final data, after analysis of the scatter, will be plotted as coefficient of expansion vs temperature up to 1000°C.

Data have been determined thus far for 4.4 and 4.8 w/o carbon sintered material and 4.8 and 5.2 w/o carbon cast specimens, but anomalies at certain temperature increments have necessitated rerunning some specimens and prevent a complete tabulation of expansion coefficient vs temperature at this time. The coefficient of linear thermal expansion has been reliably determined for nominal 4.4 sintered and 4.8 w/o carbon cast uranium carbide over the full temperature range, room temperature to 1000°C. The substoichiometric sintered material has a coefficient of 12.4×10^{-6} per °C compared to 11.5×10^{-6} per °C for the stoichiometric cast material. Two jogs in the dilation curves for all 4.4 w/o carbon sintered samples tested were seen at about 660 and 770°C, corresponding to the temperatures of α to β and β to γ transformations of uranium. The latter jog had been absent from some early curves run at higher heatup rates.

Testing of the remaining specimens is continuing and available data are being analyzed. The cause of the anomaly is believed to be known and the data are being recalculated.

2.2.2 Thermal Conductivity

Uranium carbide specimens were prepared by United Nuclear Corporation for thermal conductivity measurements to be made by another laboratory. These determinations were unsuccessful, however, because of excessive oxidation during the test. New specimens were prepared and arrangements are being made to have thermal conductivity measurements made by a new subcontractor. Determination of the coefficient of thermal conductivity will be made at a series of temperatures from about 200 to 1000°C, using a longitudinal steady state heat flow method.

2.2.3 Hot Hardness

The apparatus being used for hot hardness measurements consists of a vacuum furnace heated by molybdenum sheet resistance heating elements and a sapphire indenter attached to a molybdenum rod through which the load is transmitted. It is possible by eccentric rotation of the indenter rod and concentric rotation of the specimen to obtain a large number of indentations without opening the furnace. It is planned to run one specimen of each of the five test conditions in one furnace loading to minimize any variations due to the test conditions. At least five indentations will be made in each specimen and triplicate specimens representing each of the five test conditions will be measured. Hardness measurements will be determined up to at least 1000°C. The furnace is capable of reaching 1600°C. It is anticipated that a different indenter material will be required for temperatures above 1000°C.

The apparatus is currently being modified to permit uniform and slow application of the load by mechanized means to aid in obtaining uniform results and minimize the chance of fracturing the indenter. Upon completion of this modification, refractory metals with known hardness at temperatures up to 1000°C will be run to calibrate the apparatus prior to measuring the hot hardness of uranium carbide specimens.

2.3 EXPOSURE TESTS OF CAST URANIUM CARBIDE

The sensitivity of uranium carbide to water is well known, and it has been well established that care in handling specimens is necessary to avoid oxidation and/or hydrolysis of uranium carbide. However, there have been some conflicting reports regarding factors which may make some carbide more corrosion resistant than others and what conditions of exposure are more deleterious than others. In fact, samples handled in this laboratory did not appear to be consistent in their resistance to corrosion. Therefore, a controlled exposure test was started in October 1961. Specimens were taken at three levels of carbon content, representing nominally 4.5, 4.7 and 5.3 w/o carbon material. The specimens

were all prepared by casting and represented both ground and as-cast surface conditions. Two sets of specimens were made to test two different exposure conditions. All specimens of a given carbon content were obtained from the same casting. All specimens were thoroughly cleaned in fresh isopropyl alcohol and dried prior to the start of exposure tests. The nitrogen content of all starting material was less than 100 ppm. Oxygen analysis was not performed for the 4.5 w/o carbon material; the others were as follows:

4.7 w/o carbon - 20 ppm oxygen

5.3 w/o carbon - 60 ppm oxygen

The appearance of the starting specimens is shown in Fig. 20. Transparent specimen containers were chosen to permit continual observation. The samples in set 1 were first exposed for 60 days in an evacuated glass desiccator containing CaSO_4 as desiccant (commercially available as Drierite) while those of set 2 were exposed for the same period in a desiccator with desiccant, but were sealed off without evacuation of the container. Aside from slight darkening of the specimen surface, no change was evident after the 60-day period.

The set 1 specimens were then exposed to laboratory atmosphere without any protection. Set 2 specimens were put in a desiccator which was then evacuated and sealed; no desiccant was used.

During the next two months no changes were noticed in the appearance of the samples, but during the following three months all of the specimens in set 2 began to show surface attack. This corrosion was not severe and the product could be readily wiped off the surface without significantly altering the geometry of the sample. None of the set 1 specimens showed this attack.

During the following two months the as-cast specimens of set 2 (in vacuo) showed a gradual continuation of the surface attack evident during the previous three months. The ground specimens of set 2 also showed a continuation of a similar surface attack, but mild pitting was also noticeable. The most important

(a) Set 1, uranium carbide specimens at start of exposure test. Magnification: $3/4\times$

(b) Set 2, uranium carbide specimens at start of exposure test. Magnification $3/4\times$

Fig. 20 — Cast uranium carbide exposure test specimens at beginning of exposure test. Magnification: $3/4\times$

change occurred in the condition of the 5.3 w/o carbon specimens of set 1 (exposed to laboratory air). Transverse cracking of both the as-cast and ground 5.3 w/o carbon samples was clearly evident. The other samples of set 1 were not significantly affected. Fig. 21 shows the condition of the two sets of specimens after the seven-month exposure without using desiccant.

Thus far, there is no evidence that carbon content or surface condition has any substantial effect on corrosion behavior of cast uranium carbide stored in vacuum. A compositional effect is evident, however, in the case of specimens exposed to laboratory air. Both as-cast and ground hyperstoichiometric cast carbide showed definite transverse cracking, while the 4.5 and 4.7 w/o carbon specimens showed essentially no corrosion.

The reason for the surface attack of the specimens kept in vacuum is not clear. It is possible that this surface attack was caused by some contamination. Vapors from the mechanical pump used to evacuate the desiccator or from organic solvents used to clean the desiccator may have been the source of this contamination. These exposure tests are still in progress and will be continued to establish the effects of carbon content and surface condition on corrosion behavior of cast uranium carbide. Similar tests will be carried out for sintered specimens.

2.4 CONCLUSIONS

1. Utilizing uranium carbide powder prepared by the reaction of propane with uranium metal, sintered densities of 96 to 98% and 90 to 93% of theoretical were consistently obtained for hypo- and stoichiometric UC, respectively. The sintered material was below 1000 ppm oxygen and below 500 ppm nitrogen.
2. Preparation of skull cast uranium carbide employing feed stock obtained by reaction of UO_2 and graphite was reproducible to less than ± 0.1 w/o carbon of the desired carbon level in the range of 4.3 to 5.2 w/o carbon. Castings containing oxygen less than 200 ppm and nitrogen below 100 ppm were readily and consistently obtained. At low carbon contents (less

(a) Set 1 specimens after exposure in laboratory air (note transverse cracking of 5.3 w/o carbon specimens). Magnification: $3/4\times$

(b) View of 4.7 w/o carbon specimen from set 1 after seven-month exposure in air. Actual size.

(c) Set 2 specimens after storage in vacuum (note corrosion product from surface attack around specimens). Magnification: $3/4\times$

Fig. 21 — Cast uranium carbide exposure test specimens after seven-month exposure

than 4.5 w/o) some cracking associated with the presence of free uranium was always experienced, but was reduced by using a carbide-coated graphite mold. All castings made at all carbon levels from 4.3 to 5.3 w/o suffer from significant piping.

3. Thermal expansion measurements of nominal 4.4 w/o carbon sintered specimens and 4.8 w/o carbon cast specimens from room temperature to 1000°C showed the former had a linear expansion coefficient of 12.4×10^{-6} per °C compared with 11.5×10^{-6} for the stoichiometric cast material.
4. Exposure tests of cast uranium carbide of hypo, hyper, and stoichiometric UC revealed that carbon content was significant for samples exposed to normal laboratory air. Hyperstoichiometric carbide both with as-cast and with ground surfaces exposed to laboratory air cracked transversely after seven months. No significant damage was evident for specimens at stoichiometric and hypo stoichiometric carbon levels. Specimens stored in vacuo showed surface corrosion (mild flaking and shallow pitting) beginning after a five-months exposure and slowly progressing with exposure time. This behavior may be associated with some contamination of the storage container or specimen surface, but was not related to either carbon content or specimen surface (as-cast vs ground).

3. REFERENCES

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